Thermolysis of 2. Thermal decomposition of **2** in a condensed phase at 110° provided bicyclo[4.2.2]deca-2,4,7,9-tetraene (**6**) (53% yield), bullvalene (**7**) (46%), and others (1%). The decomposition of **2** in deuteriochloroform provided the following kinetic data: $k_{83.6^\circ} = (2.34 \pm 0.01) \times 10^{-5}$ sec^{-1}, $k_{99.6^\circ} = (1.39 \pm 0.04) \times 10^{-4}$ sec^{-1}, $\Delta H^{\ddagger} = 29$ kcal/mole, and $\Delta S^{\ddagger} = 0$ eu.

Photolysis of 2. A *ca.* 0.16 *M* solution of **2** in tetrahydrofuran-d_8 was irradiated with a 200-W high-pressure mercury lamp (Osram GmbH), using a Pyrex filter. The result (the percentage yield of each product based on the initial concentration of **2**) is shown in Table I.

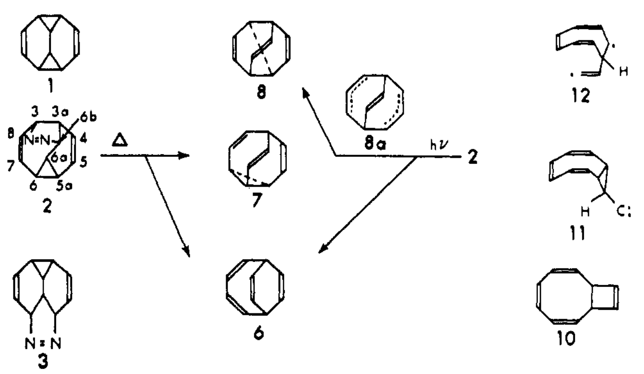


Table I

Irradiation, min	6/2 (%)	7/2 (%)	8/2 (%)
10	22.8	4.0	2.3
18	34.6	8.0	5.2
35	37.8	10.0	6.1
50	37.0	11.9	6.4
114	24.8	20.8	8.8
180	18.0	25.8	8.9

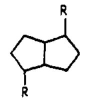
Compound **8** is tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene, and a definite structural proof is given below. It can be easily seen that pyrazoline **2** rapidly decomposed to provide **8** and **6** in a ratio of *ca.* 1:10 as the major products,[6] and the latter compound **6** underwent further photochemical conversion into **8** and **7** in a *ca.* 1:5 ratio. In fact, irradiation of **6** under identical conditions provided a very similar product distribution of **7** and **8** with approximately the same rate of formation, supporting the inference that nearly all of **7** was formed through **6** (ground state) and not directly from **2**. Compounds **7** and **8** were stable under the same conditions.

While the formation of **6** from **2** is normally expected, that the direct photoproducts of **2** are **8** and **6** deserves some comments. It is tempting to rationalize this result in terms of a diradical intermediate **8a**.[7] However, we would like to defer further discussions until deuterium-labeling experiments have been completed.

We have previously reported that photolysis of the sodium salt of bicyclo[6.1.0]nona-2,4,6-triene-*trans*-9-carboxaldehyde tosylhydrazone (**9**) afforded **6**, **8** (*vide infra*), and the major product bicyclo[6.2.0]deca-2,4,6,9-tetraene (**10**).[4] It now appears very reasonable that the carbene (**11**) generated from **9** undergoes bond cleavage to afford a diradical species **12** which leads to **8** and **6**. The absence of bullvalene (**7**) (less than 1%, if any) in the photolysate of **9** is quite consistent with this view.

Structure of 8. Catalytic hydrogenation of compound **8** provided, after uptake of 3 moles of hydrogen, a crystalline saturated compound (**13**): calculated molecular weight for $C_{10}H_{16}$, 136.1252; found, *m/e* 136.1254 (base peak).


13



14 R = CH=CH$_2$
15 R = COOH
16 R = CH$_2$OH
17 R = CH$_2$Br

Treatment of a divinyl compound (**14**)[8] with permanganate–periodate in aqueous *t*-butyl alcohol provided quantitatively a dicarboxylic acid (**15**), mp 237–238°, which was converted to a diol (**16**). The corresponding dibromide (**17**), mp *ca.* 25°, was treated with 0.5% lithium amalgam to provide a $C_{10}H_{16}$ hydrocarbon, which was identical with **13** in every respect. Therefore, compound **8** must be tricyclo[5.3.0.0^{4,8}]-deca-2,5,9-triene.[9]

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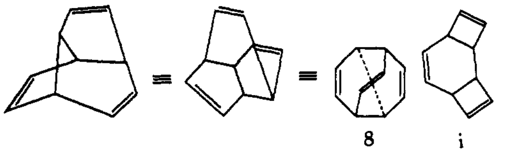
affected by the irradiation of olefinic protons and *vice versa*. This result eliminates structures isomeric to **2**, providing there is no sizeable long-range coupling between these aliphatic and olefinic protons.

(6) If the exact kinetic treatment is meaningful, then the data indicate the formation of a small amount of **7** at the initial stage of the photolysis.

(7) The thermal process of **2** leading to **7** would involve an intermediate (or possibly transition state) superficially similar to **8a** but only vibrationally excited.

(8) J. K. Crandall and C. F. Mayer, *J. Am. Chem. Soc.*, **89**, 4374 (1967).

(9) In ref 2 Jones assigned structure **8** to one of the photoproducts of **7**. On the basis of its nmr spectrum, two $(CH)_{10}$ structures, **8** and **i**, were considered, but the spectrum itself could not differentiate one from the other. Chemical information of **8** was limited and contributed very little to structural elucidation of this compound. Presumably the strongest argument in favor of structure **8** would be its infrared spectrum which is based on the assumption that the double-bond stretching band of the unknown compound **i** should appear above 1600 cm^{-1}. Therefore, the evidence was compatible with structure **8**, but further evidence was desired. Indeed, the author mentioned the progress of an X-ray crystallographic analysis of **8**.



Photolysis of the sodium salt of **9** provided, in addition to **10**, a $C_{10}H_{10}$ hydrocarbon,[5] which proved to be identical with Jones' compound by the spectral comparison. (We thank Professor M. Jones for kindly sending us an infrared spectrum.) Utilizing evidence similar to that described above, we proposed structure **8** or **i** for this compound, although some weight was given to the latter because of the structure of the major product **10** and the reaction conditions under which **8** was formed. Since then **8** has also been obtained from **2** and **6** (*vide supra*). Because of the importance of this compound in the mechanistic study of the $(CH)_{10}$ hydrocarbon isomerization, we felt it necessary to establish the structure of **9**.

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Organic Synthesis by Electrolysis. I. Electrolytic Formation of Phosphonium Ylides

Sir:

Although many methods for the preparation of phosphonium ylides have been studied, the elimination of hydrogen halide from a phosphonium halide by a strong base is the usual method of preparation. Strong bases, however, might sometimes impose a serious limitation on the preparation and subsequent reaction of the phosphonium ylide.

In the present study, we wish to report a novel method for the preparation of a phosphonium ylide from the corresponding phosphonium halide without using a strong base. A few studies have been published on the behavior of phosphonium salts in electrolytic reduction.[1,2] Although polarographic studies indicate one-electron reduction of the phosphonium salt, little is known about the detailed reaction mechanism and no attempt has been made to trap the reduction intermediate by an appropriate reactant. Recently, the electrolytic reduction of a series of ω-cyanoalkyltriphenylphosphonium salts in the presence of styrene with a mercuric cathode has been reported, and a homolytic cleavage of the carbon–phosphorus bond has been observed.[3] In our preliminary study, we found that in the electrolysis of an aqueous solution of (carbomethoxymethyl)triphenylphosphonium chloride with a carbon electrode, the corresponding ylide immediately separated on the electrode. Furthermore, the appearance of the characteristic color of the ylide at the surface of the cathode was observed in the electrolysis of a solution of methyl- or ethyltriphenylphosphonium iodide in dimethylformamide. These observations strongly suggest the formation of the phosphonium ylide at the surface of the carbon cathode.

Thus, in the present study, the electrolysis of a series of phosphonium halides in the presence of a carbonyl compound, such as benzaldehyde, butyraldehyde, or cyclohexanone, was investigated to demonstrate the formation of the phosphonium ylide. The electrolysis was carried out with a carbon electrode at 15–50 V, and the carbonyl compound was used as solvent. A fine glass filter was used between the anodic and cathodic chambers. The yields of the olefinic products are shown in the Table I. The results clearly indicate that the electrolytic method of generating phosphonium ylides from the corresponding salts is a unique and useful way of preparing the ylide without using a strong base. This method may allow the preparation of new ylides which could not be prepared by the usual technique.

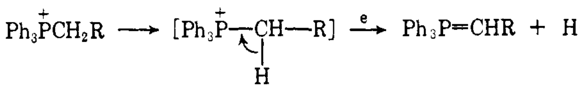
Table I. Yields of the Olefinic Products (%)[a]

Ph_3PRX		Carbonyl compound		
R	X	Benzaldehyde	Butyraldehyde	Cyclohexanone
CH_3	I	84	40[b]	
C_2H_5	I	95		15
$C_6H_5CH_2$	Br	72	95	95
CH_2COOCH_3	Cl	75	50	

[a] Yields were determined by vpc. [b] The yield may be better than that shown since the product is highly volatile.

Although sufficient experimental evidence is not available yet, two routes are conceivable for the formation of the ylide. Route 1 is the usual one-electron reduction of the phosphonium ion and route 2 is proton abstraction from the α methylene by the cathode. The formation of a small amount of benzene observed in the electrolysis of methyltriphenylphosphonium iodide might suggest a preference for route 1. Further study of the reaction and an attempt to generate sulfonium ylides by electrolysis are currently in progress.

$$Ph_3\overset{+}{P}CH_2R \xrightarrow{e} [Ph_3\dot{P}CH_2R] \longrightarrow Ph_3P{=}CHR + H\cdot \qquad (1)$$



$$Ph_3\overset{+}{P}CH_2R \longrightarrow [Ph_3\overset{+}{P}{-}\underset{\displaystyle H}{\underset{|}{C}}H{-}R] \xrightarrow{e} Ph_3P{=}CHR + H\cdot \qquad (2)$$

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The Use of Far-Infrared Spectroscopy in Characterizing Metal–Thiocyanate Bonding in Palladium(II) Complexes

Sir:

Metal–NCS or metal–SCN bonding in thiocyanate complexes has been most commonly determined[1-5] by infrared spectroscopy in the mid-infrared region.[6] The infrared spectra of palladium(II) thiocyanate complexes in this region are characterized by three absorption bands: the C–N stretching frequency which occurs below 2100 cm^{-1} for Pd–NCS and above 2100 cm^{-1} for Pd–SCN with some overlap,[2,4] the C–S stretching frequency at 860–780 cm^{-1} for Pd–NCS and 720–690 cm^{-1} for Pd–SCN,[3] and the N–C–S bending mode which has a single peak at 480–460 cm^{-1} for Pd–NCS and several peaks in the region 500–400 cm^{-1} with the most intense near 420 cm^{-1} for Pd–SCN.[7] The difficulties inherent in determining bond type based on any of these three absorptions have been pointed out by a number of authors.[1] Correlations based on the C–N stretching frequency are difficult because the variation of peak position with bond type is very small and overlap often occurs. Correlations based on the C–S stretching frequency can be uncertain because the peaks are often weak and sometimes obscured by peaks due to other ligands in the complex; also, as was pointed out by Sabatini and Bertini,[1] a peak assigned to C–S stretching in a Pd–NCS complex may actually be an overtone of the N–C–S bending mode in a Pd–SCN complex. For example, on the basis of a C–S stretching frequency of 865 cm^{-1}, the compound [Pd(py)$_2$(thiocyanate)$_2$] was thought[8] to contain N-bonded thiocyanates; however, as was later shown,[1] this peak is actually an overtone of the N–C–S bending frequency at 424 cm^{-1}, and the compound is in fact [Pd(py)$_2$(SCN)$_2$] (see Table I). Correlations based on the N–C–S bending frequencies are perhaps best, although often the peaks are weak and are sometimes obscured by absorptions due to other ligands.

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